EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Crystal structure determination of EuTiO3	**Experiment number**: HS-3895
Beamline: ID 31	**Date of experiment**: from: 18/02/2009 to: 19/02/2009	**Date of report**: 06/09/2009
Shifts: 3	**Local contact(s)**: Irene Margiolaki	*Received at ESRF:*

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$EuTiO_3$ is a quantum magnetoelectric material combining spin and charge degrees of freedom. The magnetoelectric coupling is evident from the observation of a strong enhancement of the dielectric constant as a function of applied magnetic field [1]. $EuTiO_3$ is an ideal system in which to study quantum critical fluctuations of coupled charge and spin order parameters on tuning the transition temperatures to absolute zero, and the expected emergence of novel states. As a precursor to these studies, it is essential to have a complete understanding of the normal state. Based on a lab source powder X-ray diffraction pattern, the room temperature crystal structure of EuTiO3 was reported to be Pm-3m the cubic perovskite structure with lattice parameter a=3.897 Å [2], and it was believed that it remained cubic down to the lowest temperatures. The localised 4f moments on the Eu^{2+} sites order antiferromagnetically at T_N = 5.5 K [3].

Here we report the results of the XRPD study performed at beamline ID31 of the ESRF (HS3895). Data have been collected at λ=0.4000(1) Å at RT, 150K, 50K and 5K respectively. The XRPD patterns collected as a function of *T* are displayed in Figure 1.
Unfortunately, given the limited amount of time available, it was not possible to perform a careful study of the temperature dependence. Therefore, an accurate determination of the transition temperature and order parameter evolution of the phase transition is still lacking.

The data has been analyzed by *Rietveld* method with the program GSAS and the results are summarized as follow:

(i) At room temperature, as expected, $EuTiO_3$ has a simple cubic perovskite structure with space group *Pm*-3*m*. **[3]**. Our refinement lead to satisftactory description of the data with R(F^2)=0.0408, χ^2=3.720, wRp=0.0977, Rp=0.0770). All the peaks are indexed.

(ii) At $T \leq 150$K the system undergoes a cubic to tetragonal structural phase transition (see Fig.1). The unit cell metric and the extinction conditions are consistent with either centrosymmetric *I*4/*mcm* or to non-centrosymmetric *I*4*cm* space groups. The I4/*mcm* model gives the following results at

150K: R(F^2)=0.0790, χ^2=4.594, wRp=0.1024, Rp=0.0842. Similar results can be obtain with the *I*4*cm* space group. Similar results can be obtained at 5K and are shown in Fig.2.

These results represent a big step forward in the knowledge of the structure of the sample and will give more insight in understanding the magnetoelectric properties of the material.

However, a correct assignation of the space group is fundamental to interpret correctly the coupling between the magnetic and ferroelectric order. Reciprocal space analysis carried out by means of powder diffraction alone is not adequate to exclude polar distortions. Since, the removal of the centre of symmetry allows the creation of permanent electric dipoles as a consequence of Ti and Eu displacement, the real space analysis of accurate diffraction data should shed light to the actual long range space group and/or to the eventual presence of (disordered) *polar nanoregion*.

References:

[1] T. Katsufuji and H. Takagi, Phys. Rev. B **64** (2001) 054415

[2] J. Brous et al., Acta Cryst. **6** (1953) 67

[3] C.-L. Chien et al., Phys. Rev. B **10** (1974) 3913

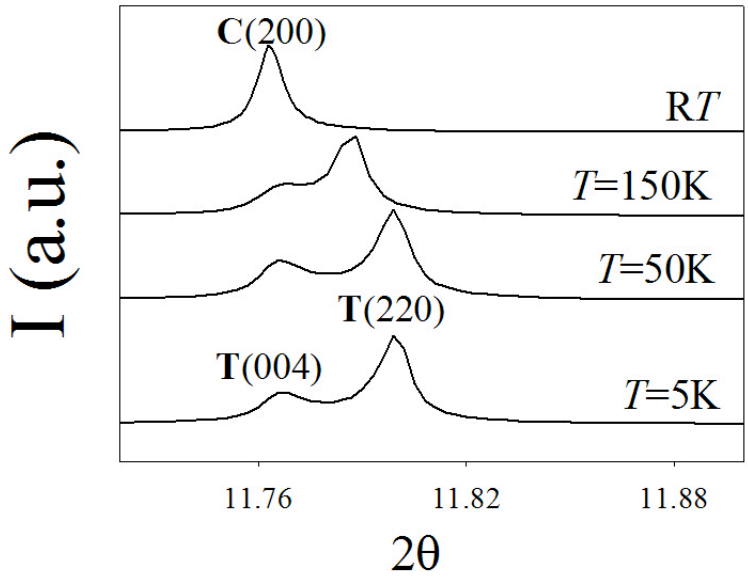

Figure 1. Details of the XRPD patterns collected at different *T* on $EuTiO_3$.The diffraction peaks **C** and **T** refer to cubic and tetragonal phases.

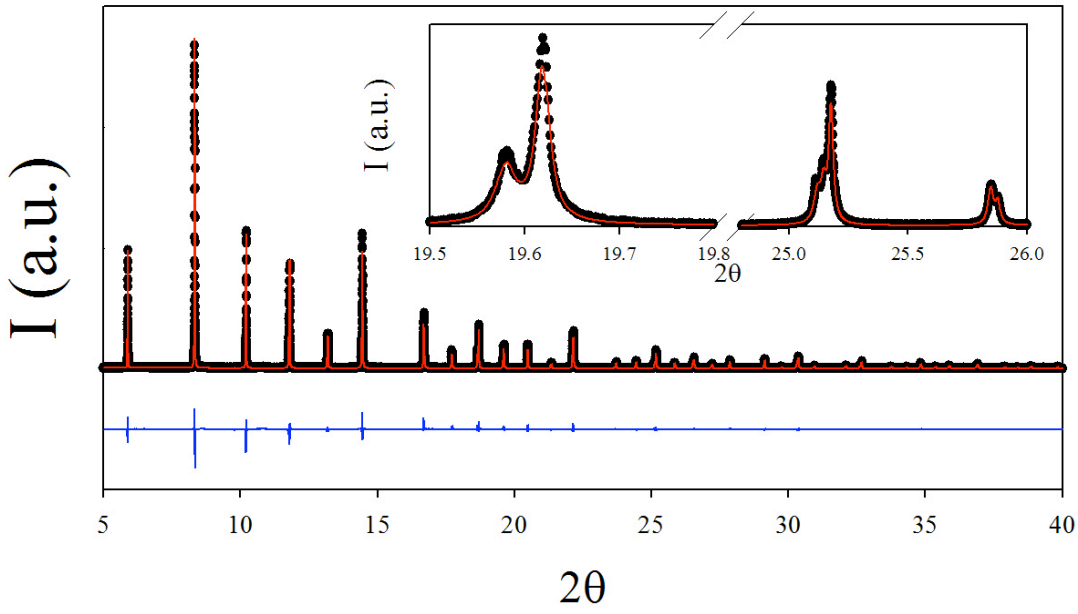

Fig.2. XRPD pattern collected at T=5K. I_{obs} (close circles), I_{calc} (red line) e $I_{obs} - I_{calc}$ (blue line). The inset shows the accuracy of the fit for some selected peaks. GoF parameters obtained with space group I4/*mcm* are R(F^2)=0.0949, χ^2=3.479, wRp=0.0943, Rp=0.0942.